

Supramolecular organization of extended benzobisoxazole cruciforms

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General Methods

All reactions were performed under nitrogen atmosphere in oven-dried glassware. Reagents were purchased from commercial suppliers and used without further purification. Solvents were used as received, except tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF), which were dried over activated alumina in an mBraun Solvent Purification System. Triethylamine (NEt₃) was distilled over KOH pellets and degassed by a 15 minute nitrogen purge prior to use. Microwave-assisted reactions were performed in a Biotage Initiator 2.0 microwave reactor, producing monochromatic microwave radiation with the frequency of 2.45 GHz.

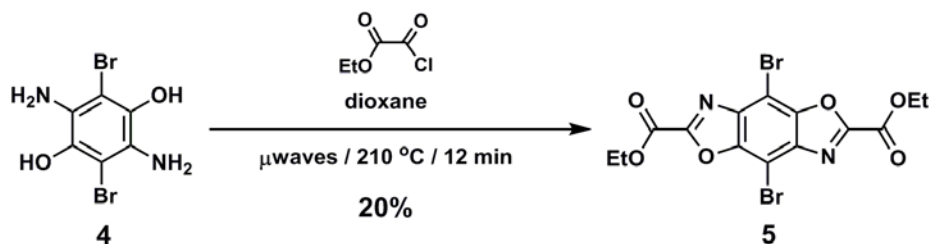
Melting points measurements were performed in open capillary tubes, using Mel-Temp Thermo Scientific apparatus, and are uncorrected. Microanalyses were conducted by Intertek USA, Inc. Mass spectral measurements were performed by the Mass Spectrometry Facility of the Department of Chemistry and Biochemistry at the University of Texas at Austin. NMR spectra were obtained on JEOL ECX-400 and ECA-500 spectrometers, with working frequencies (for ¹H nuclei) of 400 and 500 MHz, respectively. All ¹³C-NMR spectra were recorded with simultaneous decoupling of ¹H nuclei. ¹H-NMR chemical shifts are reported in ppm units relative to the residual signal of the solvent (CDCl₃, 7.26 ppm and DMSO-*d*₆, 2.50 ppm). Unless otherwise specified, all NMR spectra were recorded at 25 °C. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer using Pike MIRacle Micrometer pressure clamp. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 25 UV/Vis spectrophotometer.

Column chromatography was carried out on silica gel 60, 32–63 mesh. Analytical TLC was performed on Merck aluminum-backed silica-gel plates.

Syntheses of compounds are presented in the order following the discussion of the manuscript.

Compound numbers are identical to those in the main text of the manuscript.

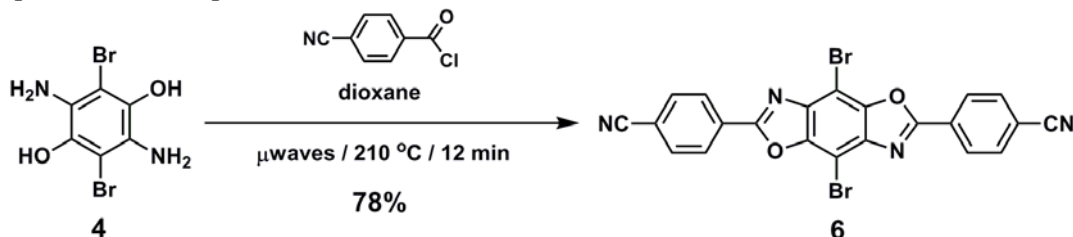
Preparation of Compound 5



A mixture of 600 mg (2.01 mmol) of 2,5-diamino-3,6-dibromobenzene-1,4-diol (**4**),¹ 0.48 mL of ethyl chloroglyoxylate (0.59 g, 4.23 mmol), and 4 mL of 1,4-dioxane was placed into a thick-walled microwave pressure vial and exposed to microwave irradiation for 12 min at 210 °C. After cooling, the mixture was slowly poured into 20 mL of 15 % K₂CO₃ solution. Precipitate was filtered, washed with H₂O, and dried in air, to give the product as a pale brownish powder (mp 270 °C, with decomposition) in 20 % yield (190 mg, 0.41 mmol).

Compound **5**: UV-Vis (CH₂Cl₂): λ_{max} (logε) = 292sh (4.18), 301 (4.36), 312 (4.40) nm. IR: 2995 (w, ν_{C-H}), 1737 (s, ν_{C=O}), 1560 (s, ν_{O-C=N}), 1150 (s, ν_{C-O}) cm⁻¹. LRMS (Cl⁺): 463. ¹H NMR (CDCl₃): δ 4.59 (q, ³J_{H-H} = 7 Hz, 4H, CH₂), 1.51 (t, ³J_{H-H} = 7 Hz, 6H, CH₃). ¹³C NMR (DMSO-*d*₆): δ 155.59, 155.12, 147.34, 140.11, 94.67, 63.72, 14.48. HRMS (Cl⁺): Calcd for C₁₄H₁₁Br₂N₂O₆⁺: 460.8984. Found: 460.8985. Anal. calcd for C₁₄H₁₀Br₂N₂O₆: C, 36.39; H, 2.18; N, 6.06. Found: C, 37.04; H, 2.05; N, 6.13.²

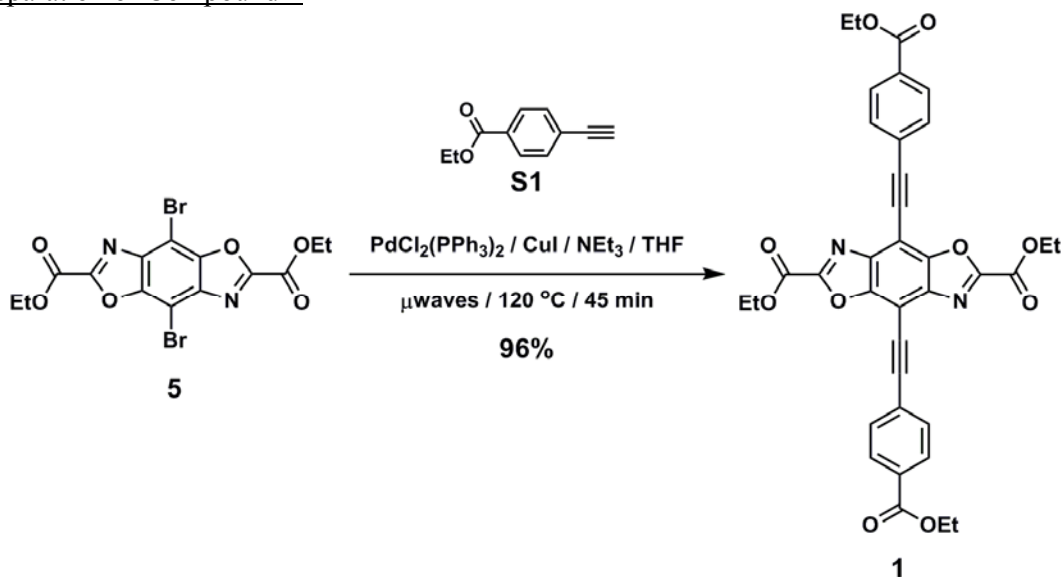
Preparation of Compound 6



A mixture of 100 mg (0.34 mmol) of 2,5-diamino-3,6-dibromobenzene-1,4-diol (**4**),¹ 166 mg of 4-cyanobenzoyl chloride (1.01 mmol), and 1 mL of 1,4-dioxane was reacted in a procedure analogous to that described for **5**, to give **6** as a brown powder (mp >330 °C) in 78 % yield (136 mg, 0.26 mmol). Compound **6** is extremely insoluble in common organic solvents, which precluded us from obtaining a meaningful ¹³C NMR spectrum.

Compound **6**: UV-Vis (CH₂Cl₂): λ_{max} (logε) = 253 (4.19), 333sh (4.41), 342 (4.56), 358 (4.63), 377 (4.44) nm. IR: 2231 (w, ν_{C=N}), 1583 (m, ν_{O-C=N}) cm⁻¹. LRMS (Cl⁺): 521. ¹H NMR (CDCl₃): δ 8.49 (d, ³J_{H-H} = 8 Hz, 4H, Ph), 7.87 (d, ³J_{H-H} = 8 Hz, 4H, Ph). HRMS (Cl⁺): Calcd for C₂₂H₉Br₂N₄O₂⁺: 518.9092. Found: 518.9096. Anal. calcd for C₂₂H₈Br₂N₄O₂: C, 50.80; H, 1.55; N, 10.77. Found: C, 51.05; H, 1.39; N, 10.72.

Preparation of Compound **1**

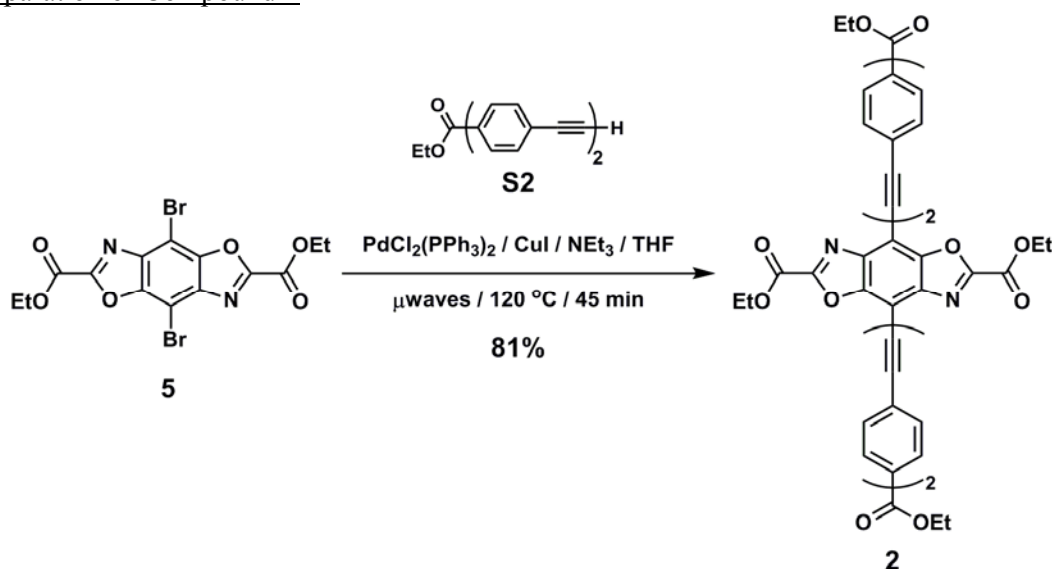


A mixture of 490 mg (1.06 mmol) of **5**, 923 mg (5.30 mmol) of ethyl 4-ethynyl benzoate (**S1**),³ 74 mg (0.11 mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$, 10 mg (0.05 mmol) of CuI , 0.90 mL (6.36 mmol) of NEt_3 , 0.4 mL of DMF, and 10 mL of THF was sealed in a thick-walled microwave pressure vial and exposed to microwave irradiation for 45 min at 120°C .

After cooling, solvents were removed under reduced pressure and the crude solid was purified by column chromatography, eluting first with a hexane/ CH_2Cl_2 (1:1) mixture, then CH_2Cl_2 , MeOH and finally with CHCl_3 to collect the product as the last, fluorescent yellow fraction. After removal of the solvent, the product was obtained as a yellow powder (mp $>220^\circ\text{C}$, with decomposition) in 96% yield (660 mg, 1.02 mmol).

Compound **1**: UV-Vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 256 (4.31), 308 (4.49), 344 (4.46), 389 (4.49), 409sh (4.37) nm. IR: 2992 (w, $\tilde{\nu}_{\text{C-H}}$), 2910 (w, $\tilde{\nu}_{\text{C-H}}$), 2216 (w, $\tilde{\nu}_{\text{C}\equiv\text{C}}$), 1746 (s, $\tilde{\nu}_{\text{C=O}}$), 1721 (s, $\tilde{\nu}_{\text{C=O}}$), 1605 (m, $\tilde{\nu}_{\text{O-C=N}}$), 1289 (s, $\tilde{\nu}_{\text{C-O}}$), 1269 (s, $\tilde{\nu}_{\text{C-O}}$) cm^{-1} . LRMS (Cl^+): 649. ^1H NMR (CDCl_3): δ 8.10 (d, $^3J_{\text{H-H}} = 8$ Hz, 4H, Ph), 7.80 (d, $^3J_{\text{H-H}} = 8$ Hz, 4H, Ph), 4.61 (q, $^3J_{\text{H-H}} = 7$ Hz, 4H, CH_2), 4.41 (q, $^3J_{\text{H-H}} = 7$ Hz, 4H, CH_2), 1.53 (t, $^3J_{\text{H-H}} = 7$ Hz, 6H, CH_3), 1.43 (t, $^3J_{\text{H-H}} = 7$ Hz, 6H, CH_3). ^{13}C NMR (CDCl_3): δ 165.97, 155.72, 154.79, 149.16, 141.25, 132.29, 131.20, 129.64, 126.41, 102.16, 101.70, 80.84, 63.96, 61.43, 14.42, 14.27. HRMS (Cl^+): Calcd for $\text{C}_{36}\text{H}_{29}\text{N}_2\text{O}_{10}^+$: 649.1822. Found: 649.1830. Anal. calcd for $\text{C}_{36}\text{H}_{28}\text{N}_2\text{O}_{10}$: C, 66.66; H, 4.35; N, 4.32. Found: C, 66.16; H, 3.46; N, 4.18.

Preparation of Compound 2

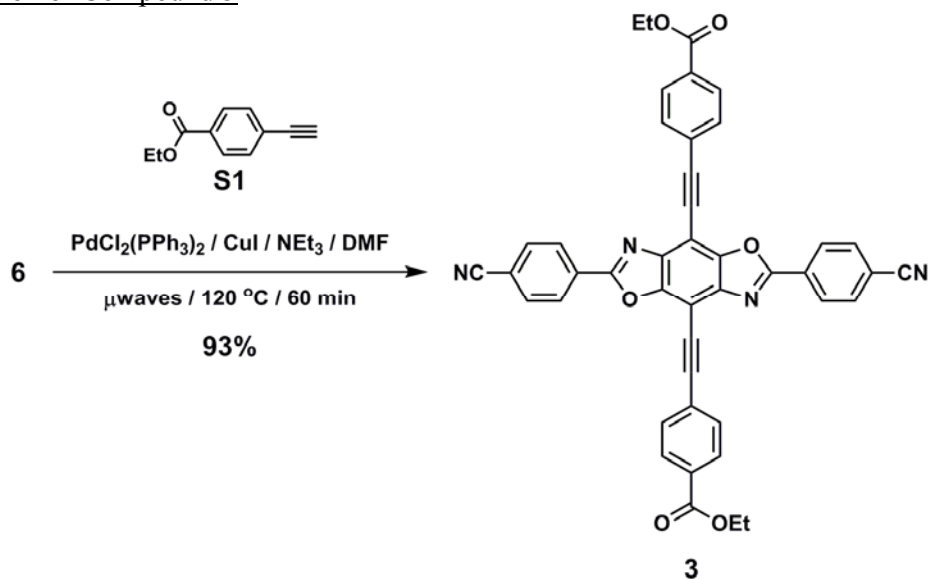


A mixture of 430 mg (0.93 mmol) of **5**, 765 mg (2.79 mmol) of ethyl 4-[(4-ethynylphenyl)ethynyl]benzoate (**S2**),⁴ 65 mg (0.09 mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$, 9 mg (0.09 mmol) of CuI , 0.78 mL (5.58 mmol) of NEt_3 , 0.4 mL of DMF, and 10 mL of THF was sealed in a thick-walled microwave pressure vial and exposed to microwave irradiation for 45 min at 120°C . After workup analogous to that described for **1**, compound **2** was obtained as a fluorescent yellow powder (mp $>240^\circ\text{C}$, with decomposition) in 81 % yield (640 mg, 0.75 mmol).

Single crystals suitable for X-ray diffraction were grown by slowly cooling a saturated solution of **2** in CH_2Cl_2 .

Compound **2**: UV-Vis (CH_2Cl_2): λ_{max} (log ϵ) = 254 (4.49), 321 (4.89), 344sh (4.71), 405 (4.68) nm. IR: 2940 (w, $\tilde{\nu}_{\text{C-H}}$), 2212 (w, $\tilde{\nu}_{\text{C}\equiv\text{C}}$), 1744 (s, $\tilde{\nu}_{\text{C=O}}$), 1711 (s, $\tilde{\nu}_{\text{C=O}}$), 1605 (m, $\tilde{\nu}_{\text{O-C=N}}$), 1276 (s, $\tilde{\nu}_{\text{C-O}}$) cm^{-1} . LRMS (Cl^+): 850. ^1H NMR (CDCl_3): δ 8.03 (d, $^3J_{\text{H-H}} = 8$ Hz, 4H, Ph), 7.73 (d, $^3J_{\text{H-H}} = 8$ Hz, 4H, Ph), 7.60–7.58 (m, 8H, Ph), 4.61 (q, $^3J_{\text{H-H}} = 7$ Hz, 4H, CH_2), 4.38 (q, $^3J_{\text{H-H}} = 7$ Hz, 4H, CH_2), 1.52 (t, $^3J_{\text{H-H}} = 7$ Hz, 6H, CH_3), 1.39 (t, $^3J_{\text{H-H}} = 7$ Hz, 6H, CH_3). ^{13}C NMR (CDCl_3 , 55°C): δ 165.98, 155.74, 154.84, 149.27, 141.22, 132.33, 131.79, 131.58, 130.43, 129.58, 127.54, 124.17, 122.39, 102.60, 101.76, 91.74, 91.33, 80.55, 63.67, 61.14, 14.31, 14.16. HRMS (Cl^+): Calcd for $\text{C}_{52}\text{H}_{37}\text{N}_2\text{O}_{10}^+$: 849.2448. Found: 849.2442. Anal. calcd for $\text{C}_{52}\text{H}_{36}\text{N}_2\text{O}_{10} \cdot 0.25\text{CH}_2\text{Cl}_2$ (molecular formula derived from the single-crystal X-ray structure): C, 72.13; H, 4.23; N, 3.22. Found: C, 72.09; H, 4.05; N, 3.18.

Preparation of Compound 3



A slurry of 100 mg (0.19 mmol) of **6**, 134 mg (0.77 mmol) of ethyl-4-ethynyl benzoate (**S1**),³ 13 mg (0.02 mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$, 2 mg (0.01 mmol) of CuI, 0.16 mL (1.15 mmol) of NEt_3 , and 4 mL of DMF was sealed in a thick-walled microwave pressure vial and exposed to microwave irradiation for 60 min at 120°C .

After cooling, the mixture was filtered on a Büchner filter funnel. Yellow-brownish crude material was washed with hexane and a small amount of THF, until brownish coloration was no longer noticeable. Then, the yellow precipitate was dissolved in a large amount of CH_2Cl_2 , leaving only a very small amount of insoluble material on the filter. After CH_2Cl_2 removal, 126 mg (0.178 mmol, 93%) of yellow, fluorescent powder (mp $>330^\circ\text{C}$) was obtained.

Single crystals suitable for X-ray diffraction were grown by slowly cooling a saturated solution of **3** in CH_2Cl_2 .

Compound **3**: UV-Vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 246 (4.59), 317sh (4.68), 337 (4.78), 383 (4.98), 409sh (4.71) nm. IR: 2927 (w, $\tilde{\nu}_{\text{C-H}}$), 2229 (w, $\tilde{\nu}_{\text{C=N}}/\tilde{\nu}_{\text{C=C}}$), 1718 (s, $\tilde{\nu}_{\text{C=O}}$), 1606 (m, $\tilde{\nu}_{\text{O-C=N}}$), 1276 (s, $\tilde{\nu}_{\text{C-O}}$) cm^{-1} . LRMS (Cl^+): 707. ^1H NMR (CDCl_3): δ 8.53 (d, $^3J_{\text{H-H}} = 8$ Hz, 4H, Ph), 8.15 (d, $^3J_{\text{H-H}} = 8$ Hz, 4H, Ph), 7.89 (d, $^3J_{\text{H-H}} = 8$ Hz, 4H, Ph), 7.85 (d, $^3J_{\text{H-H}} = 8$ Hz, 4H, Ph), 4.43 (q, $^3J_{\text{H-H}} = 7$ Hz, 4H, CH_2), 1.45 (t, $^3J_{\text{H-H}} = 7$ Hz, 6H, CH_3). ^{13}C NMR (CDCl_3 , 55°C): δ 165.84, 163.02, 149.21, 141.63, 132.79, 132.06, 131.29, 130.28, 129.69, 128.60, 126.77, 117.90, 115.80, 100.48, 99.56, 81.68, 61.33, 14.33. HRMS (Cl^+): Calcd for $\text{C}_{44}\text{H}_{27}\text{N}_4\text{O}_6^+$: 707.1931. Found: 707.1929. Anal. calcd for $\text{C}_{44}\text{H}_{26}\text{N}_4\text{O}_6 \cdot 1.5\text{CH}_2\text{Cl}_2$ (molecular formula derived from the single-crystal X-ray structure): C, 65.52; H, 3.50; N, 6.72. Found: C, 65.92; H, 2.99; N, 6.85.

Crystal Data for Compound 2

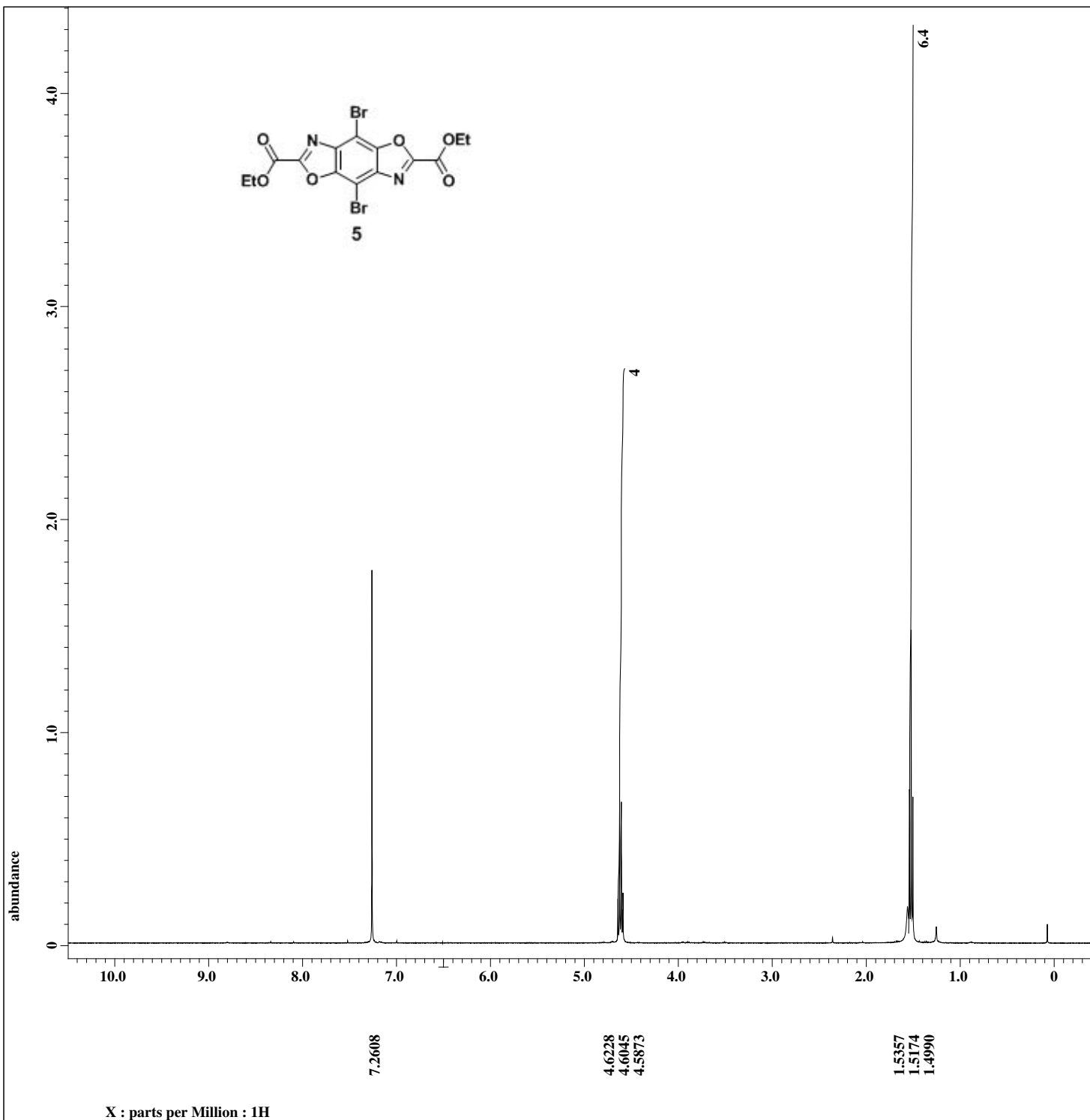
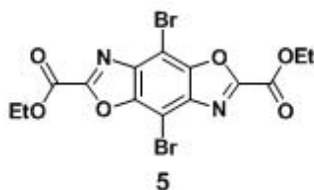
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Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1} - C_i^1$ (No. 2)	
Unit cell dimensions	$a = 8.987(2)$ Å	$\alpha = 99.874(3)^\circ$
	$b = 9.998(2)$ Å	$\beta = 93.339(3)^\circ$
	$c = 14.506(3)$ Å	$\gamma = 107.320(3)^\circ$
Volume	1217.6(4) Å ³	
Z	1	
Density (calculated)	1.389 Mg/m ³	
Absorption coefficient	0.306 mm ⁻¹	
F(000)	526	
Crystal size	0.38 × 0.09 × 0.04 mm ³	
Theta range for data collection	3.93° to 25.00°	
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -17 ≤ l ≤ 17	
Reflections collected	9381	
Independent reflections	4259 [$R_{int} = 0.027$]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000 and 0.858	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4259 / 0 / 324	
Goodness-of-fit on F ²	1.021	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.081$, $wR_2 = 0.186$	
R indices (all data)	$R_1 = 0.109$, $wR_2 = 0.200$	
Largest diff. peak and hole	0.46 and -0.40 e ⁻ /Å ³	

Crystal Data for Compound 3

Empirical formula	C ₄₆ H ₃₀ Cl ₄ N ₄ O ₆	
Formula weight	876.54	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 3.8598(5) Å	$\alpha = 105.228(2)^\circ$
	b = 14.4562(17) Å	$\beta = 94.344(2)^\circ$
	c = 18.4857(22) Å	$\gamma = 93.861(2)^\circ$
Volume	988.3(2) Å ³	
Z	1	
Density (calculated)	1.473 Mg/m ³	
Absorption coefficient	0.357 mm ⁻¹	
F(000)	450	
Crystal color and shape	Yellow flat column	
Crystal size	0.35 × 0.10 × 0.05 mm ³	
Theta range for data collection	1.47° to 25.06°	
Limiting indices	-4 ≤ h ≤ 4, -17 ≤ k ≤ 16, 0 ≤ l ≤ 21	
Reflections collected / unique	5050 / 3470 [R _{int} = 0.0535]	
Completeness to theta = 25.06°	98.5 %	
Absorption correction	Empirical	
Max. and min. Transmission	0.9861 and 0.8237	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2081 / 0 / 281	
Goodness-of-fit on F ²	1.025	
Final R indices [I > 4σ(I)]	R ₁ = 0.0501, wR ₂ = 0.1200	
R indices (all data)	R ₁ = 0.0811, wR ₂ = 0.1418	
Largest diff. peak and hole	0.378 and -0.344 e ⁻ /Å ³	

References

- 1 L. S. Hegedus, R. R. Odle, P. M. Winton and P. R. Weider, *J. Org. Chem.*, 1982, **47**, 2607.
- 2 For this and other compounds that gave elemental analyses outside of the ±0.4% range, copies of ¹H and ¹³C NMR spectra are attached at the end of Electronic Supporting Information.
- 3 (a) M. Belema, V. N. Nguyen and F. C. Zusi, *Tetrahedron Lett.*, 2004, **45**, 1693. (b) E. Yashima, T. Matsushima and Y. Okamoto, *J. Am. Chem. Soc.*, 1997, **119**, 6345.
- 4 T. Funaki, H. Sugihara, K. Kasuga, K. Osamu, N. Onosawa, M. Yanagida and Y. Kawanishi, *Jpn. Kokai Tokkyo Koho*, 2008.

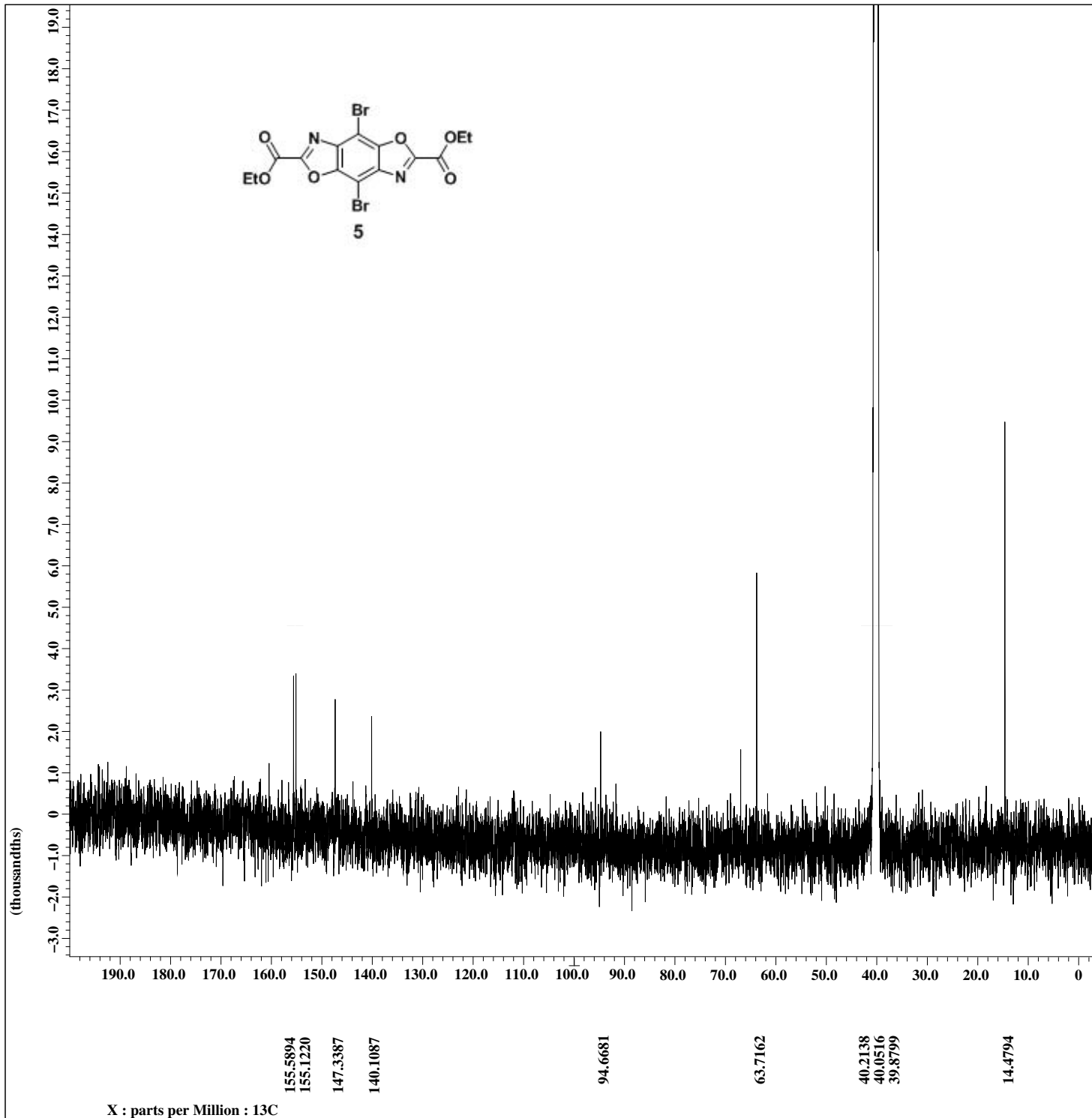
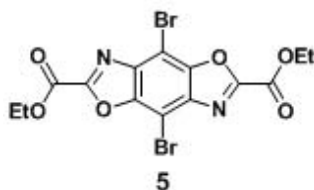


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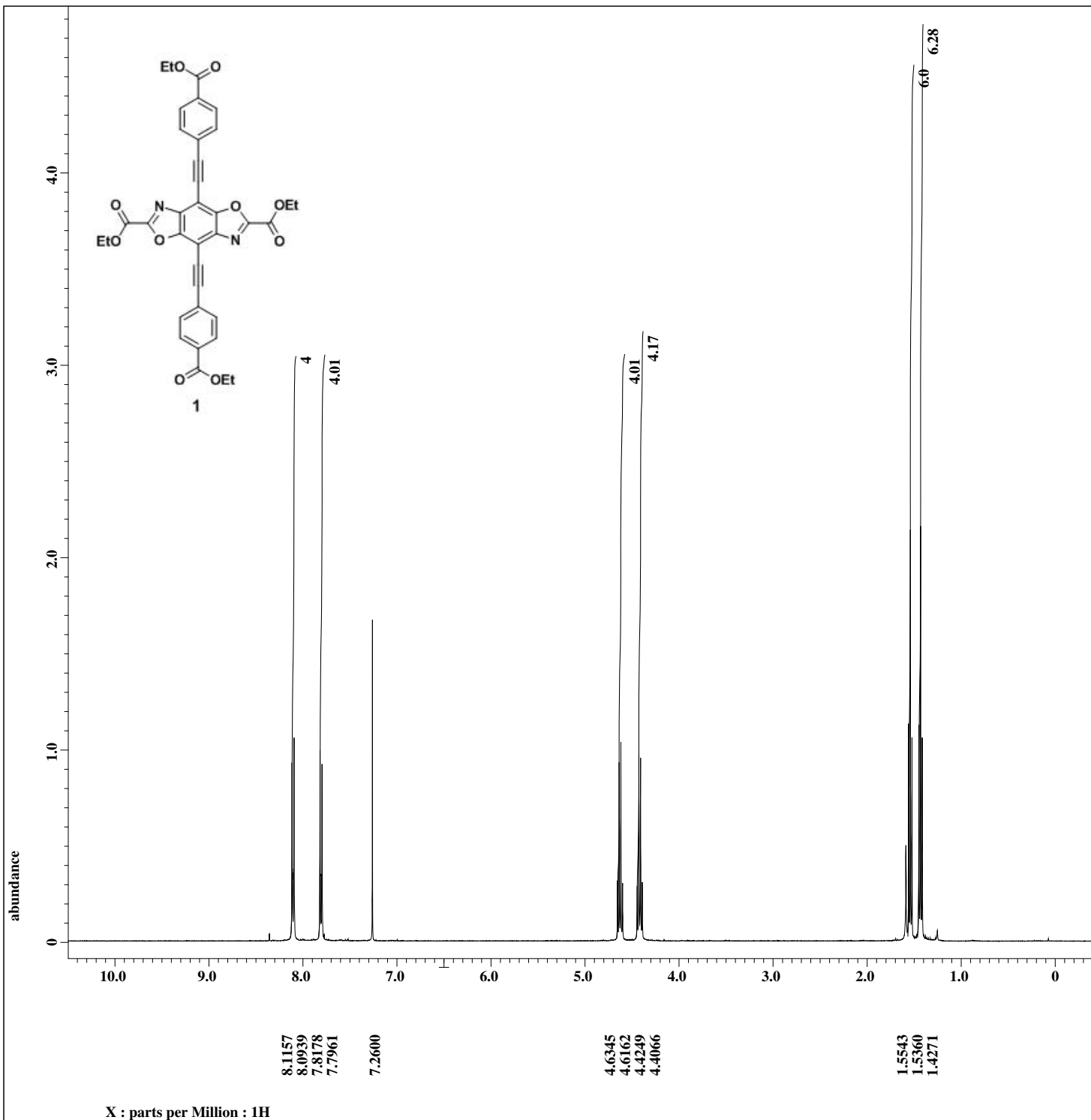
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Peak at 66.88 ppm
corresponds to 1,4-dioxane,
which was used as the solvent
in the reaction.



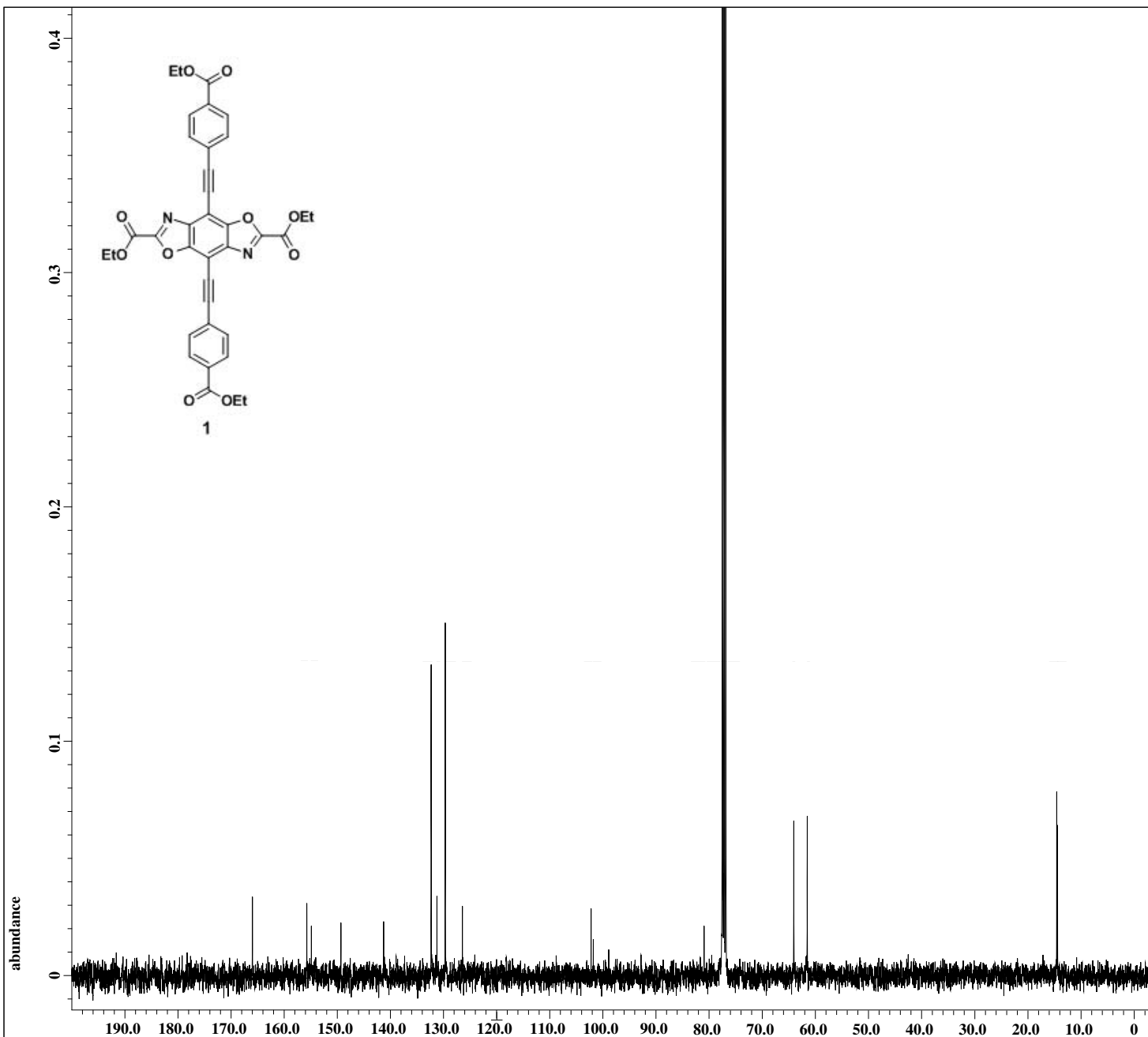
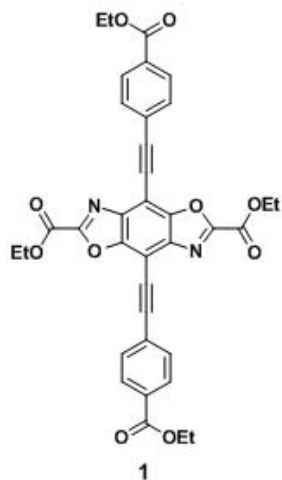
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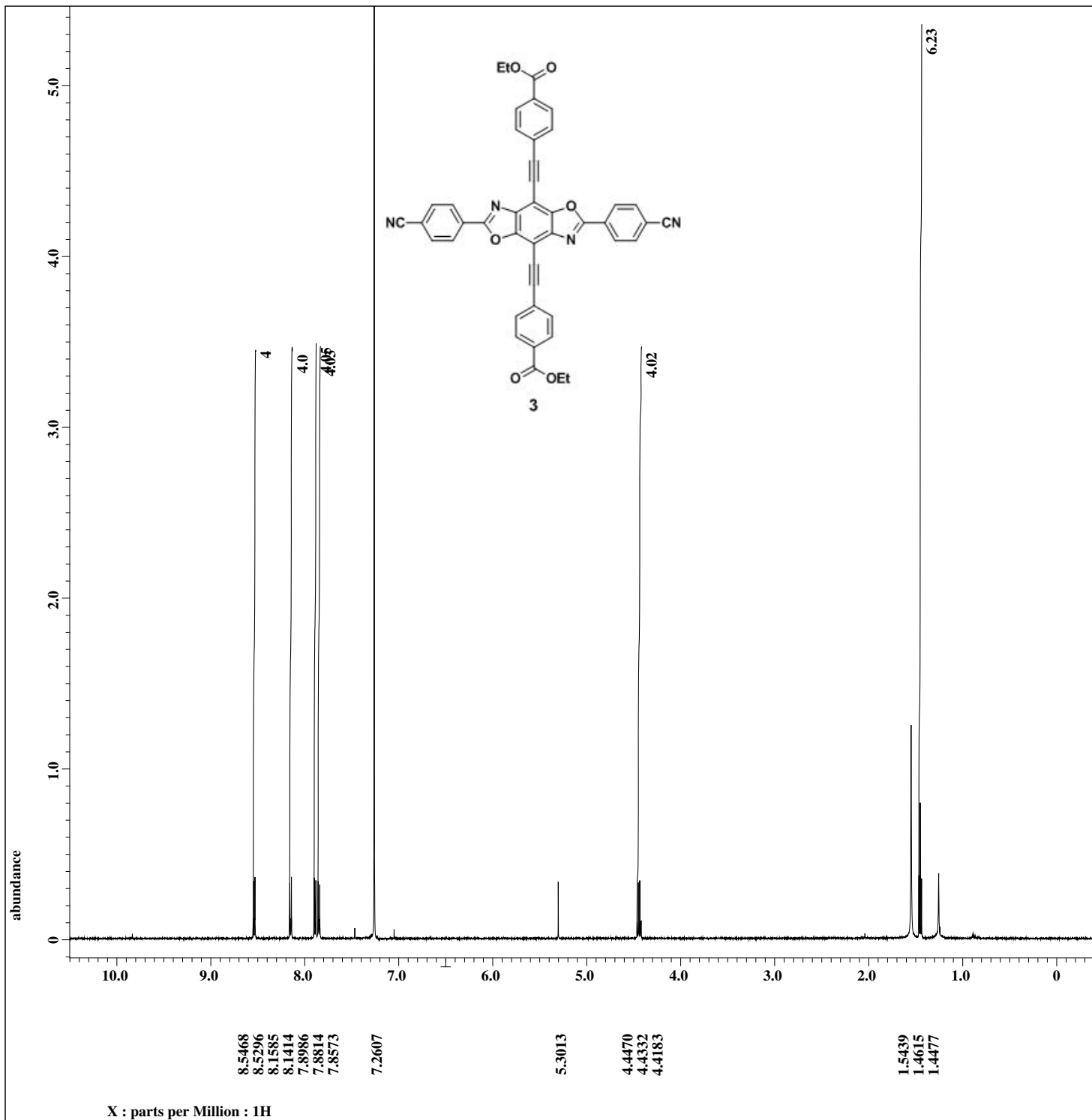
Comment = single pulse decouple
Data_format = 1D_COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 400P
Spectrometer = DELTA2_NMR

Field_strength = 9.389766[T] (400 [MHz])
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333 [MHz]
X_offset = 120 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665 [Hz]
X_sweep = 31.40703518 [kHz]
Irr_domain = 1H
Irr_freq = 399.78219838 [MHz]
Irr_offset = 5 [ppm]
Clipped = TRUE
Mod_return = 1
Scans = 1066
Total_scans = 1066

X_90_width = 12.4525 [us]
X_acq_time = 1.04333312 [s]
X_angle = 30 [deg]
X_atn = 6 [dB]
X_pulse = 4.15083333 [us]
Irr_atn_dec = 22 [dB]
Irr_atn_noe = 22 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 1 [s]
Recvr_gain = 60
Relaxation_delay = 1 [s]
Repetition_time = 2.04333312 [s]
Temp_get = 21.9 [dC]

165.9758
155.7261
154.8680
149.2998
141.2526
132.2901
131.2031
129.6395
126.4072
102.1608
101.7413
80.8701
77.4281
77.1039
76.7893
63.9653
61.4291
14.4236
14.2710

X : parts per Million : 13C



Filename = KO-3-H
Author = miljanic
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 4-JAN-2010 16:35:46
Revision_time = 23-MAR-2010 14:12:36
Current_time = 23-MAR-2010 14:13:27

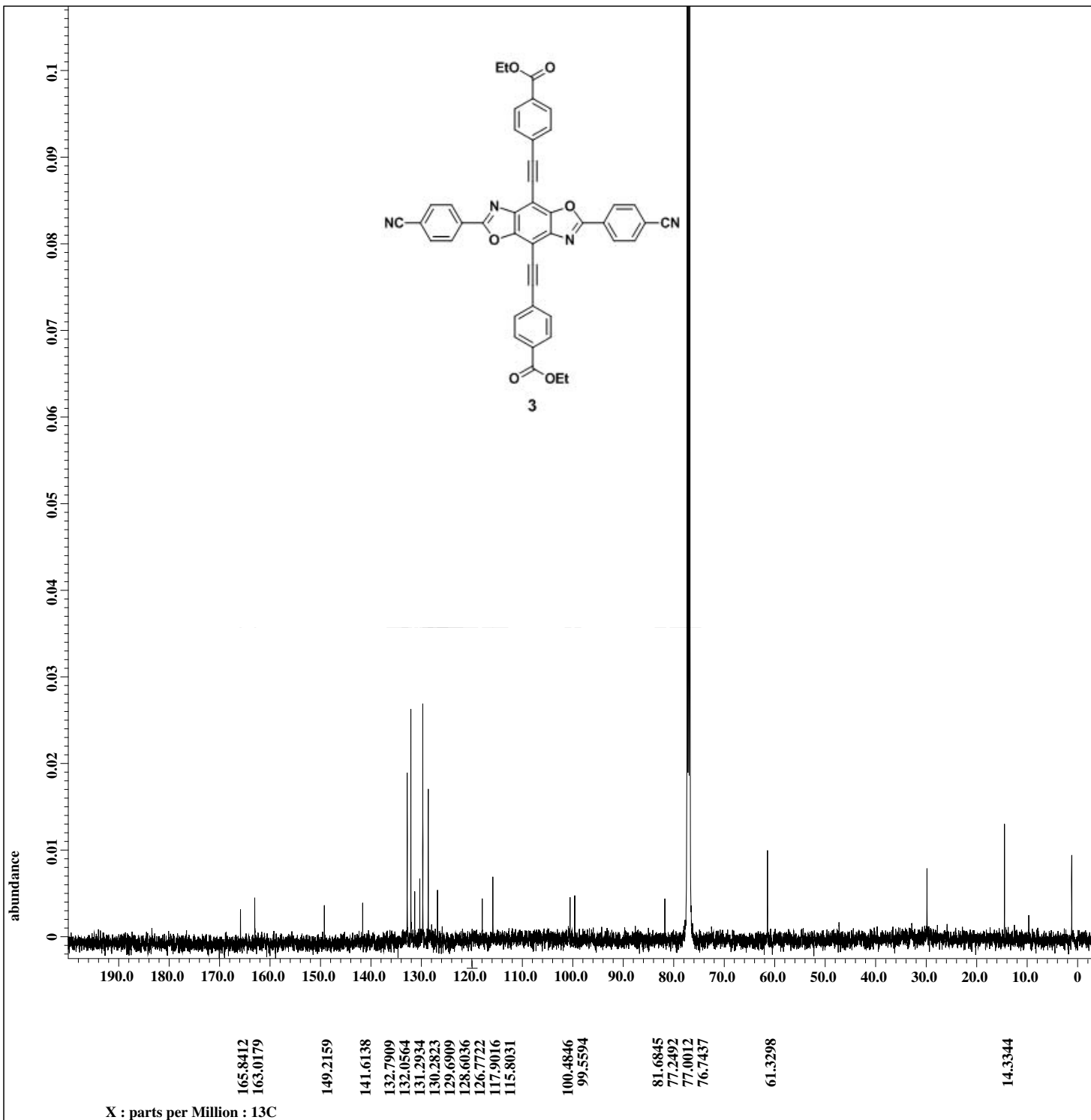
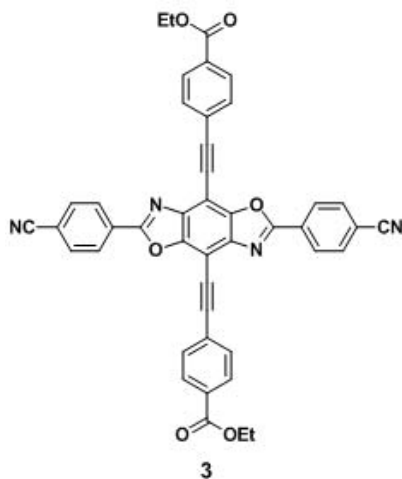
Comment = single_pulse
Data_format = 1D_COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA_500
Spectrometer = ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 6.5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 32
Total_scans = 32

X_90_width = 11.45[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 3[dB]
X_pulse = 5.725[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 58
Relaxation_delay = 1[s]
Repetition_time = 2.74587904[s]
Temp_get = 21.4[dc]

Peak at 5.30 ppm comes from the solvent of crystallization (dichloromethane), as confirmed by X-ray diffraction. Peak at 1.54 ppm comes from water, and the peak at 1.48 corresponds to an unidentified impurity.

X : parts per Million : 1H



```
Filename      = KO-3-C
Author       = miljanic
Experiment    = single_pulse_dec
Sample_id    = 1
Solvent      = CHLOROFORM-D
Creation_time = 10-DEC-2009 08:22:30
Revision_time = 23-MAR-2010 14:16:42
Current_time  = 23-MAR-2010 14:17:30

Comment      = single pulse decouple
Data_format  = 1D_COMPLEX
Dim_size     = 26214
Dim_title    = 13C
Dim_units    = [ppm]
Dimensions   = X
Site        = ECA_500
Spectrometer = ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain       = 13C
X_freq         = 125.76529768[MHz]
X_offset       = 120[ppm]
X_points       = 32768
X_prescans    = 4
X_resolution   = 1.19959034[Hz]
X_sweep        = 39.3081761[kHz]
Irr_domain     = 1H
Irr_freq       = 500.15991521[MHz]
Irr_offset     = 5.0[ppm]
Clipped        = FALSE
Mod_return     = 1
Scans          = 25044
Total_scans    = 25044

X_90_width    = 11.77[us]
X_acq_time    = 0.83361792[s]
X_angle       = 30[deg]
X_atn         = 9[dB]
X_pulse       = 3.92333333[us]
Irr_atn_dec   = 19.5[dB]
Irr_atn_noe   = 19.5[dB]
Irr_noise     = WALTZ
Decoupling    = TRUE
Initial_wait  = 1[s]
Noe           = TRUE
Noe_time      = 1[s]
Recvr_gain    = 60
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get      = 55[dC]
```

Peaks at 29.70 and 0.99 ppm come from an impurity extracted from the NMR tube caps by deuterated chloroform at high temperature and prolonged recording times. This is a well-documented problem: <http://tinyurl.com/yktxyzm>